

RESEARCH COMMUNICATIONS

the intracellular killing of leishmania, trypanasoma and *M. bovis*^{1,2,15}. Both human monocytes and mouse macrophages when treated with IFN- γ completely eliminate *Toxoplasma gondii*. Similarly TNF- α , is also known to enhance the antimycobacterial nature of macrophages^{17,18}. In our experiments, human monocytes upon treatment with TNF- α , IFN- γ , LPS and PMA together handled *M. tuberculosis* in a similar way as untreated monocytes.

Many workers have used calcitriol either alone or in association with other cocktail of cytokines to enhance the antimycobacterial nature of human monocytes in *vitro*^{19,20}. But there are also controversial reports about the elevated levels of calcitriol in serum samples from tuberculosis patients²¹. Therefore we were hesitant to perform an experiment with calcitriol as one of the macrophage activating agents. Further, recently Davies et al.²² have shown that a combination of TNF- α , IFN- γ and calcitriol at optimum concentration failed to enhance the antimycobacterial nature of the human monocytes. It is generally assumed that elimination of *M. tuberculosis* from tissues of protected individuals depends on destruction of the organisms by macrophages that are activated by lymphokines derived from T lymphocytes. The right combination of cytokines that activates macrophages and the right *in vitro* condition to demonstrate the antimycobacterial nature of human monocyte has been a matter of debate for a long time.

In our observations, human monocytes inhibit the growth and multiplication of *M. tuberculosis* in *vitro* till 72 h, after which *M. tuberculosis* multiply inside the intracellular environment of monocytes. TNF- α , IFN- γ , LPS and PMA stimulate the intracellular respiratory burst in macrophages, but fail to inhibit the growth of intracellular mycobacteria.

Recently Molloy et al.²³ highlighted that tuberculosis infection is controlled by granulomatous response and this is intimately associated with accumulation, activation and death of mononuclear leucocytes. Molloy et al. pointed out that cell death could be due to necrosis or apoptosis and provided further data to show that only during apoptosis (induced by ATP), but not necrosis, of chronically infected cells, 60-70% loss in intracellular viability of BCG resulted. They assumed that observations made on one Mycobacterium species are relevant to another. On the contrary, when we treated *M. tuberculosis* or *M. smegmatis* infected human monocytes with ATP, we observed loss in monocyte viability confirming apoptosis with no reduction in bacterial viability. The reason for this discrepancy is under investigation.

We conclude that there is no killing of *M. tuberculosis* by unstimulated or cytokine stimulated and ATP-treated human monocyte derived macrophages in *vitro*.

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Identification of a new parameter, At(T), controlling the thermally induced effects on Kevlar 49 fibres

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The magnitude of the thermally-induced changes in the crystallinity, weight, tensile strength, and surface damages in Kevlar 49 fibres is controlled by the duration of each and individual thermal exposure, At(T). Several short exposures cause less damage to the fibre than a single long exposure. This observation is user-relevant.

OUR earlier investigations¹ on Kevlar 49 fibres showed that exposure to thermal environments lead to changes in the structural as well as the tensile characteristics of these fibres. The observed structural changes were:

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(i) macro changes such as surface damages and weight loss and (ii) changes at the level of the crystal lattice. These two types of changes were found to be closely related. The most prominent crystal structural change introduced by thermal exposures was reduction in crystallinity of the fibres. Among the tensile properties, strength was found to be more sensitive to thermal exposures than modulus. Thus it was shown that the effect of thermal exposures on Kevlar fibres was always controlled by two parameters; the temperature, T , and the duration of the cumulative exposure to T , $t_{\text{cum}}(T)$. Moreover, it was established that the two parameters always act in unison. Changes introduced at any temperature, T_2 , were shown to recur at a temperature $T_1 (< T_2)$, if the exposure to T_1 was sufficiently long¹. Further studies on $T-t_{\text{cum}}(T)$ correlation have led to recognition of isothermal decomposition behaviour of Kevlar fibres at temperatures far below the reported decomposition temperature, T_d , of 500/550°C (refs 3,4). The study on the isothermal decomposition behaviour showed that the residual X-ray crystallinity of the heat-treated fibres could be reliably used as a parameter to assess the extent of degradation. Degradation preceding decomposition was found to be accompanied by a progressive reduction, and an eventual total loss in crystallinity. Details of these observations have been presented elsewhere⁵. While evaluating the residual crystallinity of heat-treated fibres, it was observed that in addition to the earlier-mentioned parameters T and $t_{\text{cum}}(T)$, a third parameter, $\Delta t(T)$ —the duration of an individual exposure to T —also critically influenced the crystallinity of the fibres. This letter presents the details of this observation.

As shown in equation (1), the cumulative exposure of the fibres to any temperature T is likely to be made up of several short exposures of the type Δt_1 , Δt_2 , etc., which can be represented as:

$$t_{\text{cum}}(T) = \Delta t_1(T) + \Delta t_2(T) + \Delta t_3(T) + \dots \quad (1)$$

However, when the exposures are of equal durations,

$$t_{\text{cum}}(T) = n \cdot \Delta t(T), \quad (2)$$

where n is an integer.

The present study concerns the identification of the role of $\Delta t(T)$, based primarily on the values of X-ray crystallinity, which are further supported by observations on other parameters such as weight loss, tensile strength, and surface damage. The samples used were Kevlar 49 fibres made commercially available by DuPont Inc. USA. The effect of Δt was studied at $T=250, 300, 400$ and 500°C respectively, in air. It must be pointed out that of these, 250 and 300°C are within the service range of temperatures recommended for Kevlar⁶. For conducting accelerated tests, the temperatures 400 and 500°C which are beyond the recommended service range were also

included. The choice of $t_{\text{cum}}(T)$ values, though arbitrary, was such as to ensure that detectable changes in fibre characteristics were introduced for those exposures. For a chosen set of T and $t_{\text{cum}}(T)$ values, the fibres were subjected to exposures of equal duration (eqn. 2).

While exposures to 250 and 300°C were carried out using an air circulating oven, for 400 and 500°C a tubular resistance furnace was used. In these arrangements the temperatures could be controlled and maintained to an accuracy of ± 5 and 2° respectively. After each heating, the samples were air cooled for at least 45 min and the cumulative exposure was further continued. Equatorial X-ray diffraction patterns from fibres, both prior to and at the end of completing the selected duration of cumulative exposure, $t_{\text{cum}}(T)$, were recorded using a Philips powder diffractometer. Copper $K\alpha$ radiation and a graphite monochromator in the diffracted beam were used. Samples were rotated at the rate $\frac{1}{4}^\circ$ per min and the chart speed was 10 mm per min. The diffraction patterns were restricted to the 2θ range of 15 to 27° which included the two most intense reflections in the diffraction pattern from Kevlar, (200) and (110). Relative changes in crystallinity were obtained from the total integrated intensities⁷ estimated from the respective areas under the diffraction profiles measured using a digitizer and an Autocad system. The weight loss incurred was estimated from the weights of the sample measured both prior to and after a chosen heat treatment respectively. A sartorius analytical balance capable of reading upto 0.0001 g was used for weighing of the samples. Tensile testing of single filaments was carried out on a zwick universal testing machine. Filaments ≈ 25 mm in gauge length were pulled under tension at the rate of 2.5 mm per min. The chart speed used was 60 mm per min. For each experiment, at least 50 filaments were examined and the average value was worked out. For observing the surface characteristics of fibres, Jeol scanning electron microscope was used.

Figure 1 compares the diffraction profiles recorded from the two samples both of which were exposed to

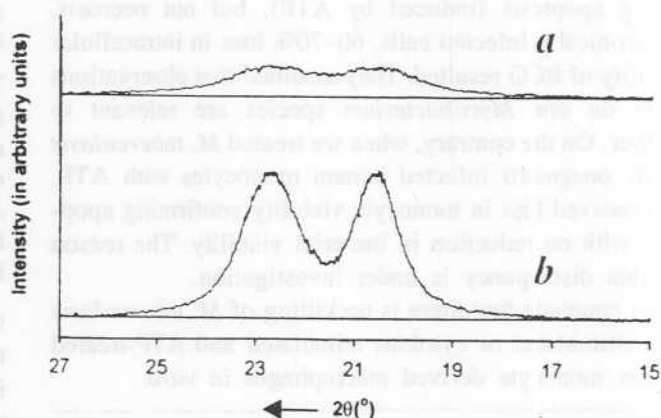


Figure 1. Comparison of diffraction profiles from fibres exposed to 400°C for 10 h: a, $n=1$; and b, $n=4$.

400°C for 10 h. While the pattern in Figure 1 *a* is from the sample exposed continuously for 10 h i.e., $n = 1$, the pattern in Figure 1 *b* is from the sample exposed for the same 10 h, but in four successive steps, each of 2.5 h duration. As expected^{1,2,5,8}, in both the cases there is a drop in crystallinity, but in the former, the drop is as much as $\approx 80\%$, while in the latter, it is only $\approx 50\%$. The other experimental conditions being the same, the observed difference in the residual crystallinity could perhaps be attributed exclusively to the difference in the $\Delta t(T)$ values. Similar behaviour has been observed at other temperatures as well. Figures 2 and 3 present the data corresponding to $T = 500$ and 300°C respectively. At 500°C , the sample that was exposed continuously for 0.5 h showed a drop in its crystallinity by $\approx 70\%$ (Figure 2 *a*), and in contrast, the observed drop is only $\approx 20\%$ when in the same sample, although exposed for 0.5 h, the exposures were given in six separate steps, each of five minutes duration. At 300°C the reductions in crystallinity values are by 42% and 8% for n values of 1 and 12 respectively. Figure 4 depicts the consolidated data on the residual crystallinity of fibres exposed to 300, 400 and 500°C respectively. It must be emphasized

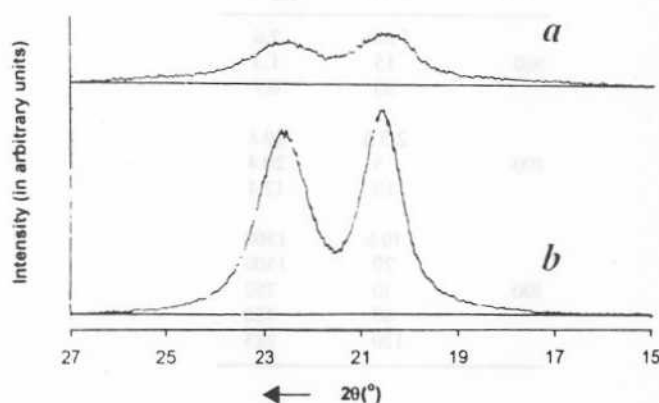


Figure 2. Comparison of diffraction profiles from fibres exposed to 500°C for 0.5 h: *a*, $n = 1$; and *b*, $n = 6$.

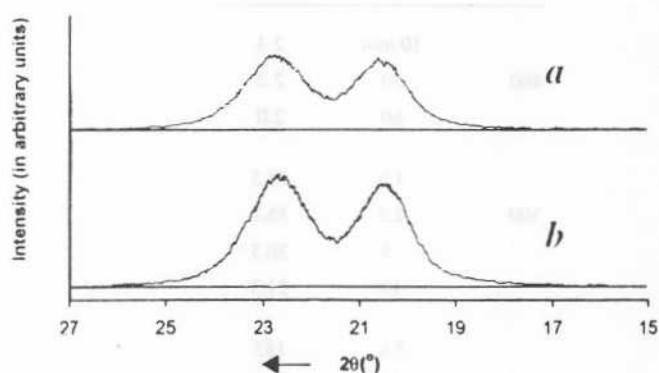


Figure 3. Comparison of diffraction profiles from fibres exposed to 300°C for 120 h: *a*, $n = 1$; and *b*, $n = 12$.

at this point that in these curves, each of the data points represents the treatment of the sample for the entire cumulative exposure selected for that temperature. For example, in the curve corresponding to 500°C , all the three data points represent completion of the 0.5 h of cumulative exposure. The difference, however, lies in the route chosen to reach the $t_{\text{cum}}(T)$ value. Values of n marked near each data point describe these differences. $n = 6$ and 2 represent reaching the cumulative exposure of 0.5 h via a total of 6 and 2 steps, each of 5 and 15 min duration respectively. It must be mentioned that the X-ray data corresponding to 250°C have not been included, since at this comparatively lower temperature, the onset of changes in the initial crystallinity was quite delayed, requiring exposures of several hundreds of hours. However, the available data at 300, 400 and 500°C provide unambiguous evidence for the role of $\Delta t(T)$ on the residual crystallinity of heat-treated fibres.

Having established the role of $\Delta t(T)$ on crystallinity, it was of interest to know whether it influenced other thermally-induced changes as well, i.e. the effect of $\Delta t(T)$ on weight loss, reduction in tensile strength, and surface damages were also examined. Interestingly, these parameters also manifested a dependence on the $\Delta t(T)$ values, the details of which are given below. Figure 5 illustrates the dependence of isothermally-induced weight loss on the $\Delta t(T)$ values. At 400°C , a single exposure of 15 h duration led to $\approx 96\%$ weight loss whereas when the same 15 h of exposure was covered in five steps each of 3 h duration, the observed weight loss was only $\approx 40\%$. Similar differences observed at 500 and 300°C are also included in Figure 5. As in the case of crystallinity, the data corresponding to 250°C have not been included due to the delay in the onset of changes.

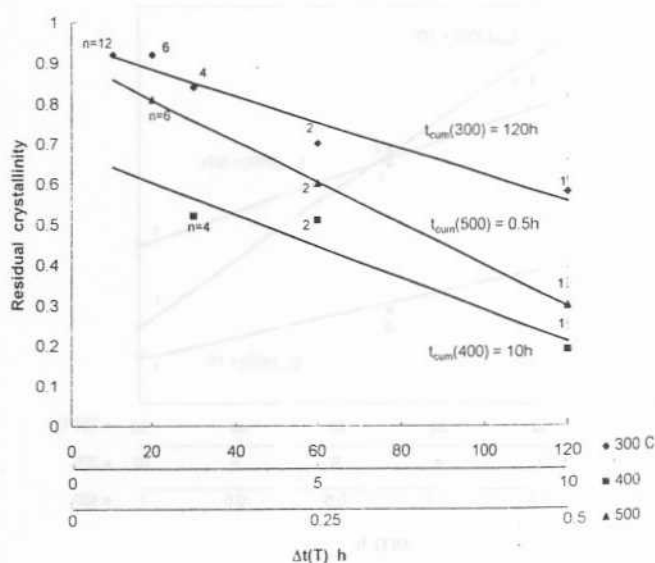


Figure 4. Effect of $\Delta t(T)$ on the residual crystallinity of the fibre. Values of n have also been marked.

Figure 6 records the effect of $\Delta t(T)$ on tensile strength. It was observed that 10 h of continuous exposure to 300°C reduces the tensile strength to ≈ 1.7 GPa, whereas after completing ten separate exposures, each of 1 h duration, the tensile strength is retained as ≈ 2.5 GPa. It must be pointed out that in Figure 6, the observed crossing of the curves corresponding to 250 and 300°C is due to the difference in the $t_{cum}(T)$ values. With dissimilar $t_{cum}(T)$ values, the slopes of the curves are not directly comparable. As the fibres exposed to 500°C had turned slightly brittle, they could not be handled comfortably for tensile testing. Hence, the tensile data corresponding to 500°C had not been collected. The

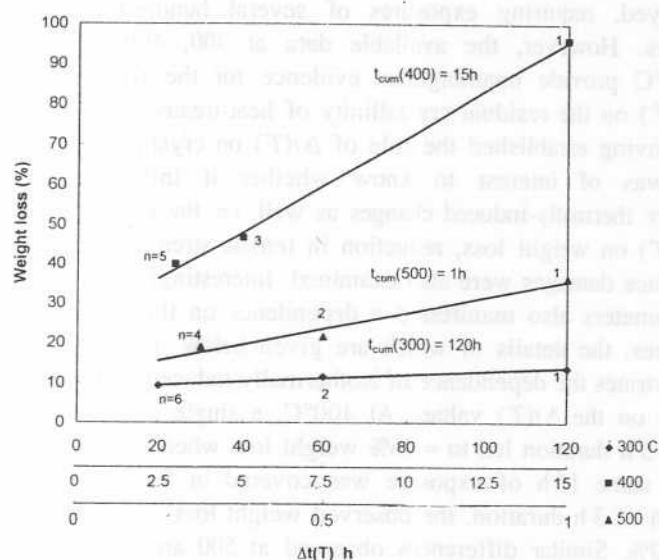


Figure 5. Effect of $\Delta t(T)$ on the thermally-induced weight loss. Values of n have also been marked.

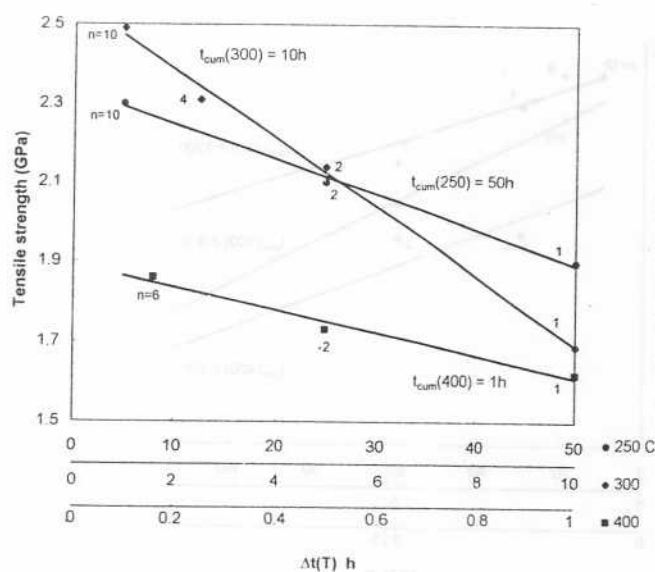


Figure 6. Effect of $\Delta t(T)$ on tensile strength. Values of n have also been marked.

present data on reductions in crystallinity, weight, and tensile strength (Figures 4–6) further show that for any chosen combination of the T and $t_{cum}(T)$ values, the thermally-induced changes in all the three parameters are linearly dependent on the $\Delta t(T)$ values.

The data presented in Figures 4 and 6 may also be extrapolated to provide information on the duration of the cumulative exposure needed to reach the zero crystallinity and zero tensile strength states, t_{cum}^{zero} . Tables 1 and 2 list the values of t_{cum}^{zero} for the various T and $\Delta t(T)$ obtained by assuming linear extrapolation. It is obvious that for a chosen value of T , selection of comparatively smaller values of $\Delta t(T)$ delays reaching the zero crystallinity and zero tensile strength states.

Figures 7 and 8 illustrate the effect of $\Delta t(T)$ on the thermally-induced surface damages. It is conspicuous that the minute holes formed on the surface of fibres exposed to 400°C for 10 h in a single, long exposure are far more numerous (Figure 7a) than when the same exposure is given in four steps (Figure 7b). Likewise, the longitudinal splitting observed on the surface of

Table 1. Extrapolated values of t_{cum}^{zero} for crystallinity

$T(^{\circ}\text{C})$	$\Delta t(T)$	$t_{cum}^{zero} \text{ (h)}$
500	5 min	2.6
	15	1.3
	30	0.7
400	2.5 h	20.8
	5	20.4
	10	12.4
300	10 h	1500
	20	1500
	30	750
	60	400
	120	285

Table 2. Extrapolated values of t_{cum}^{zero} for tensile strength

$T(^{\circ}\text{C})$	$\Delta t(T)$	$t_{cum}^{zero} \text{ (h)}$
400	10 min	2.4
	30	2.2
	60	2.0
300	1 h	45.5
	2.5	35.7
	5	30.3
	10	21.3
250	5 h	185
	25	143
	50	125

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fibres exposed to 300°C for 120 h is deeper on continuous exposure (Figure 8a) compared to when it was split into twelve separate exposures (Figure 8b). Thus, as in crystallinity, weight loss, and tensile strength; the surface characteristics also exhibit a dependence on the $\Delta t(T)$ values. These observations provide ample evidence that the role of $\Delta t(T)$ on the thermally-induced effects on

Kevlar is indeed of a generalized nature. Thus for all the parameters examined, it was observed that several short exposures totaling to a cumulative exposure of $t_{\text{cum}}(T)$, cause less damage to the fibre than a single long exposure of the same duration t_{cum} to T .

Admittedly, at this stage of the analysis, no attempt is being made to understand the micro mechanism

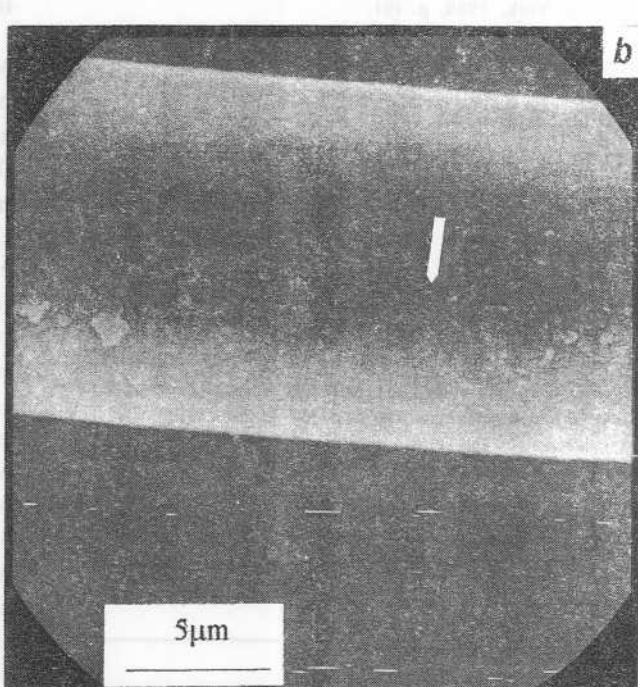
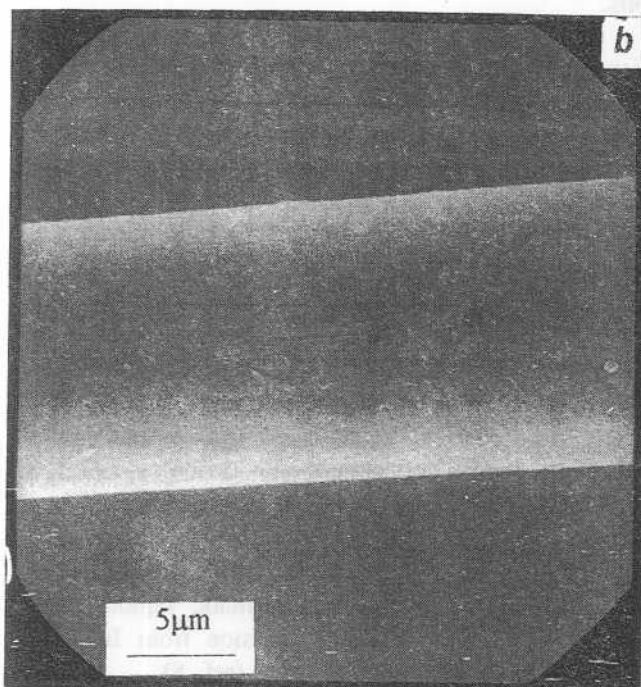
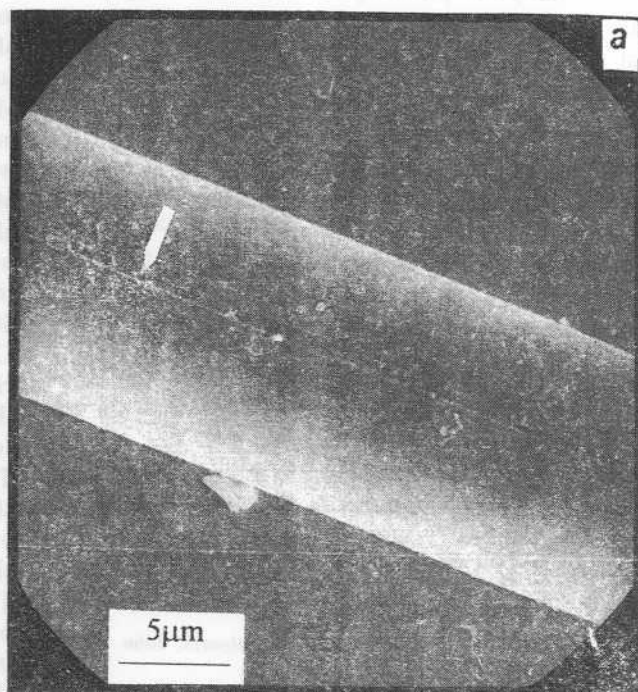
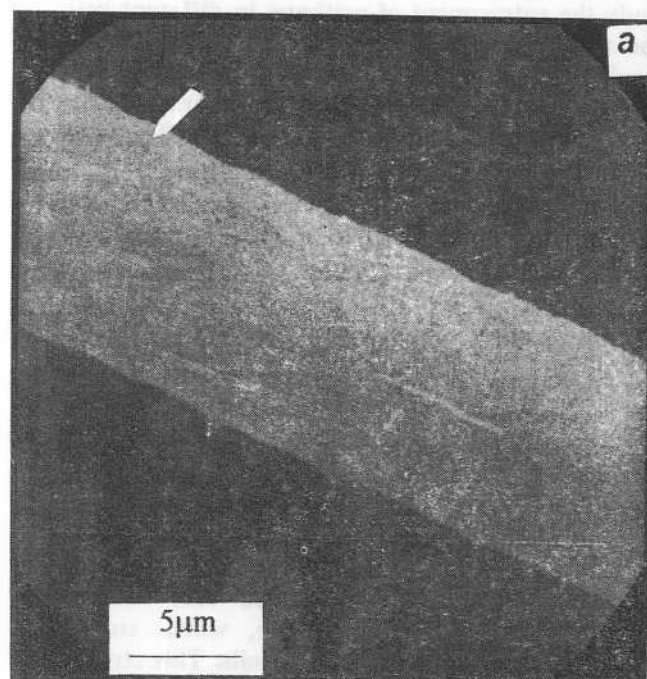


Figure 7. Scanning electron micrograph showing the formation of minute holes on the surface of fibre exposed to 400°C for 10 h: *a*, $n=1$; and *b*, $n=4$. Arrow shows a typical hole.

Figure 8. Scanning electron micrograph showing the thermally-induced longitudinal splitting (indicated by the arrow) on the surface of fibre exposed to 300°C for 120 h: *a*, $n=1$; and *b*, $n=12$.

underlying the observations on the effect of $\Delta t(T)$. Further experimental data are perhaps required to throw light in understanding the changes – structural and others – which are responsible for the present observations. It must be emphasized that the results on the effect of $\Delta t(T)$ are presented in this article primarily from a user's point of view. Kevlar is a fibre with high temperature applications, and exposure to elevated temperatures have been shown to result in several types of deterioration^{1,2,5,8}. The results which have emerged from the present study are primarily user-relevant. They provide the useful information that if the fibres are to be used at elevated temperatures, the onset of thermally-induced deterioration can be delayed or their severity can be lessened by splitting a single long exposure into several short exposures. From a judicious choice of the $\Delta t(T)$ values, delaying the decay of the exceptional initial characteristics of the fibre can be successfully achieved. Basically, a 'go slow' approach at elevated temperatures would prove advantageous. Our data also prompt us to suggest that when the high temperature properties are compiled, the role of $\Delta t(T)$ should also be mentioned.

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Methane entrapment in different rice soils of India

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Part of methane produced in submerged paddy field is trapped in the soil, thereby reducing its emission into the atmosphere. Keeping the importance of methane entrapment in view, an experiment was undertaken to study the entrapment of methane in different soils of India. An incubation study was carried out with soils collected from rice fields at ten different locations of India for 60 days to determine the entrapment of methane in the soils during this period. The soils were incubated under submerged condition, at 30°C. Methane entrapment/day as well as the total amount of methane entrapped in the 60-day study period were observed to be different for the different soils. The total entrapment varied from 0.139 to 80.578 $\mu\text{g CH}_4 \text{ g}^{-1}$ soil, and from 0.212 to 91.959 $\mu\text{g CH}_4 \text{ g}^{-1}$ soil, when the same soils were treated with rice straw. The soils entrapped 13.04 to 72.32% of the total methane produced, while in the straw treated soils the entrapment ranged from 9.35 to 68.17%. Total and percent entrapment of methane did not show any significant relationship with the sand, silt, or clay content of the soils, while they showed significant correlation with total methane production. This suggests that there could be other factors operating, other than soil texture, which control methane entrapment in submerged soils. This stresses the need for further studies on methane entrapment in soils.

METHANE (CH_4) is one of the important gases contributing to the greenhouse effect. It is increasing at an average global atmospheric concentration of about 0.016 ppmV yr^{-1} (about 1% yr^{-1}) and CH_4 concentration in the troposphere is currently about 1.75 ppmV (ref. 1). Data from polar ice cores indicate an approximately exponential increase in tropospheric methane concentrations over the past 300 years². This increase may be contributing to a rise in global temperature due to relatively high absorption of infrared radiation by CH_4 (ref. 3). Total annual global emission of methane is estimated to be 420–620 Tg yr^{-1} (ref. 4). Wetland rice agriculture is the major anthropogenic source of it, and emissions from this source are estimated at 60–170 Tg yr^{-1} , representing 25% of the worldwide release⁵, at 25–100 Tg yr^{-1} (ref. 6) and at 20–150 Tg yr^{-1} (ref. 7). Studies covering the various agroclimatic regions of India have shown that methane emission from Indian rice fields is not more than 4 Tg yr^{-1} (ref. 8).

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